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(71)Applicant : ASAHI CHEM IND CO LTD

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(72)Inventor : TSUBATA TOSHIO
AMANO HATSU

(54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To enhance the discharge characteristic of a battery, and sharply reduce the irreversible capacity reduction of the battery in the storage at high temperature by setting the specific surface area of a positive electrode active material, the average particle size of a primary particle, the average particle size of a secondary particle, and the porosity of an electrode to specified ranges, respectively.

SOLUTION: Li used for a positive electrode active material of battery $\text{Li}(\text{Li}_x\text{Mn}_{2-x})\text{O}_4$ ($0 < x \leq 0.18$) has a BET specific surface value by nitrogen adsorption of 1.5 m²/g or less, preferably, 1.1-1.5 m²/g. The size of a primary particle is thus set to 0.5-5 μm . The average particle size of a secondary particle is set to 5-30 μm , preferably, 5-25 μm . Further, the porosity of an applied positive electrode is set to 15-40%. To make the specific surface area of the positive electrode active material to 1.5 m²/g or less, a first thermal treatment of 800-900°C is required, and it is important to further perform a second thermal treatment at about 500-700°C. When the second thermal treatment is not performed, a phase other than an intended matter such as Li_2MnO_3 , Mn_3O_4 or the like is apt to be left.

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CLAIMS

[Claim(s)]

[Claim 1] The negative electrode which comes to **** a lithium ion occlusion and the active material which can be emitted, It is a nonaqueous electrolyte rechargeable battery possessing the positive electrode which comes to **** the nonaqueous electrolyte of lithium ion conductivity, and the active material which consists of a spinel system lithium manganese multiple oxide expressed with the following general formula. The nonaqueous electrolyte rechargeable battery characterized by for the BET specific surface area of this positive active material being below 1.5m²/g, for the mean particle diameter of a primary particle being 0.5 micrometers - 5 micrometers, and for the mean particle diameter of an aggregated particle being 5 micrometers - 30 micrometers, and the voidage of this positive electrode being 15% - 40%.

Li(Li_x Mn_{2-x}) O₄ (however, 0 < x ≤ 0.18)

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the improvement of the discharge property of a nonaqueous electrolyte rechargeable battery, and an elevated-temperature preservation property which used the spinel system lithium manganese multiple oxide for positive active material.

[0002]

[Description of the Prior Art] In recent years, high-performance-izing of electronic equipment, especially a cordless device and small lightweight-ization are progressing by the technical progress of the electronics field, and especially the spread of a camcorder/movie, a notebook sized personal computer, cellular phones, etc. is remarkable. The rechargeable battery carried in these devices in connection with this is a source of power for realizing the further high performance device, and since it is in the heart of the product which influences the engine performance of the device itself, its demand of high-capacity-izing, lightweight-izing, etc. is strong. Also in it, since a nonaqueous electrolyte rechargeable battery especially the nonaqueous electrolyte rechargeable battery using the active material which can carry out occlusion emission of the lithium ion as a negative electrode, and the so-called rechargeable lithium-ion battery are high voltages, its energy density is high, and it is the rechargeable battery expected most.

[0003] In the positive active material of a rechargeable lithium-ion battery, the multiple oxide of a lithium and cobalt, the multiple oxide of a lithium and nickel, the multiple oxide of a lithium and manganese, etc. are known as an object which can carry out occlusion emission of the lithium with 4V class potential to the oxidation reduction potential of a metal lithium, and Kamiichi especially of the multiple oxide of a lithium and cobalt has already been carried out from each company as a cell.

[0004] However, cobalt has the anxiety it becomes insufficient in the future supplying, when [expensive] it is an element. On the other hand, manganese does not have the anxiety that supply is insufficient, either, and since it is a low price, it becomes possible to offer broadly a cheap and highly efficient nonaqueous electrolyte rechargeable battery to the need of the further nonaqueous electrolyte rechargeable battery. For this reason, although many researches have been done to the multiple oxide of a lithium and manganese, the region of utilization is not yet arrived at.

[0005] Spinel structure is taken, if a crystal lattice carries out expansion contraction, collapse of the crystal structure tends to take place and charge and discharge are repeated by charge and discharge for this reason, cycle stability will fall, and it is supposed that a capacity fall starts a lithium manganese multiple oxide. On the other hand, at JP,7-97216,A or JP,7-245106,A, by the conventional manufacture approach, since the surface area of an active material becomes comparatively small and crystallinity becomes high, it thought that the crystal had become is easy to be destroyed with the lithium ion insertion and balking at the time of charge and discharge, and the problem solving has been measured by carrying out a BET specific surface area more than 3m²/g. However, since the contact part of an active material and the electrolytic solution will become large if it has the problem that manganese tends to be eluted when a lithium manganese multiple oxide contacts the electrolytic solution, and specific surface area becomes large, manganese tends to be eluted, when especially left under an elevated temperature 80 degrees C or more, a remarkable capacity fall arises, and the satisfying nonaqueous electrolyte rechargeable battery is not obtained.

[0006]

[Problem(s) to be Solved by the Invention] Its safety is high, and using the positive electrode which ****(ed) the cheap lithium manganese multiple oxide, the purpose of this invention has a good discharge property, is a high

energy consistency, and even after being further left under an elevated temperature by it, it is to offer a nonaqueous electrolyte rechargeable battery with the good cell engine performance.

[0007]

[Means for Solving the Problem] This invention is a nonaqueous electrolyte rechargeable battery characterized by being the nonaqueous electrolyte rechargeable battery characterized by providing the following, and the BET specific surface area of this positive active material being below $1.5\text{m}^2/\text{g}$, the mean particle diameter of a primary particle being 0.5 micrometers - 5 micrometers, and the mean particle diameter of an aggregated particle being 5 micrometers - 30 micrometers, and the voidage of this positive electrode being 15% - 40%. The negative electrode which comes to **** a lithium ion occlusion and the active material which can be emitted Nonaqueous electrolyte of lithium ion conductivity The positive electrode which comes to **** the active material which consists of a spinel system lithium manganese multiple oxide expressed with the following general formula

[0008] $\text{Li}(\text{Li}_x\text{Mn}_{2-x})\text{O}_4$ (however, $0 < x \leq 0.18$)

When occlusion emission of the lithium is carried out by charge and discharge, change of the valence of manganese takes place and the spinel mold lithium manganese multiple oxide used as positive active material of this invention not only carries out expansion contraction at the time of charge and discharge, but contains the trivalent manganese said to be unstable in that case. Such unstable manganese is untied into the electrolytic solution, and is considered to be a broth and a cone. If the elution of manganese happens, when the positive active material itself will deteriorate, in order to have a bad influence also on a negative electrode or the electrolytic solution, the positive active material of this invention reduces a manganese content trivalent by transposing some manganese to a lithium, and is stopping the elution of manganese to the minimum. Therefore, x of $\text{Li}(\text{Li}_x\text{Mn}_{2-x})\text{O}_4$ has the desirable range of $0 < x \leq 0.18$, and it is $0.05 \leq x \leq 0.15$ more preferably. Since capacity will fall remarkably if x exceeds 0.18, it is not desirable. Moreover, in order for trouble to be in the cycle engine performance and to make the cycle engine performance good, as for 0.05 or more, x is desirable at $x = 0$. this invention persons result that both of elevated-temperature preservation properties of a nonaqueous electrolyte rechargeable battery and discharge properties become good in a header and this invention by controlling the voidage when making the particle size of a specific primary particle and an aggregated particle, and it into an electrode, as a result of advancing research on the lithium manganese multiple oxide expressed with such general formula $\text{Li}(\text{Li}_x\text{Mn}_{2-x})\text{O}_4$.

[0009] The BET specific surface area by the nitrogen adsorption process is below $1.5\text{m}^2/\text{g}$, and $\text{Li}(\text{Li}_x\text{Mn}_{2-x})\text{O}_4$ used for the positive active material of the cell of this invention are $0.1\text{m}^2/\text{g}$ - $1.5\text{m}^2/\text{g}$ still more preferably. In the case of the lithium manganese multiple oxide which a primary particle condenses and forms the aggregated particle although specific surface area will generally become small if mean particle diameter becomes large, it changes with temperature by which the particle size of the primary particle which does effect dominant in specific surface area is heat-treated, and it is difficult heat treatment temperature for it for the particle size of a primary particle to be small and to make the whole specific surface area small at about 400-650 degrees C. Since a permutation would not be enough performed if it heat-treats at an about 800-950-degree C elevated temperature when a lithium permutes some manganese of a lithium manganese multiple oxide conventionally, it needed to heat-treat at the temperature of about 400-650 degrees C. Therefore, it was difficult for a lithium to permute some manganese enough and to make specific surface area below into $1.5\text{m}^2/\text{g}$. It found out that it was possible for this invention persons to permute some manganese with a lithium enough when it heat-treats on condition that specification, and to make specific surface area below into $1.5\text{m}^2/\text{g}$. Although a discharge property improves because the touch area of a lithium manganese multiple oxide and the electrolytic solution becomes large when specific surface area exceeds $1.5\text{m}^2/\text{g}$ (i.e., when a primary particle is small), and it considers as an electrode, the cell property after elevated-temperature preservation falls greatly. Moreover, in order to make specific surface area below into $0.1\text{m}^2/\text{g}$, it is necessary to enlarge primary particle size. For this reason, a touch area with the electrolytic solution decreases and a discharge property falls. Therefore, in order to make specific surface area into request within the limits, the magnitude of a primary particle has 0.5 micrometers - desirable 5 micrometers.

[0010] Moreover, it depends for the mean particle diameter of an aggregated particle on the particle size of a start raw material greatly. 5 micrometers - 30 micrometers of 5 micrometers - 25 micrometers of mean particle diameter of the aggregated particle of the positive active material used for the cell of this invention are 5 micrometers - 20 micrometers still more preferably preferably. When mean particle diameter is less than 5 micrometers, a discharge property improves, but since the cell property after elevated-temperature preservation falls, it is not desirable. Moreover, if larger than 30 micrometers, a discharge property will worsen. Furthermore, in order to create an electrode, coating in various approaches is performed, but since the homogeneity of the paste itself -- a lithium

manganese multiple oxide sediments in the state of the paste used for coating -- will not be acquired, or a blur will arise on the front face of the film by which coating was carried out and a uniform paint film will not be obtained if an average particle is large, it is not desirable. Furthermore, the positive electrode of the cell of this invention must be the paint film whose voidage is 15% - 40%. The opening into which the electrolytic solution can sink substantially is the thing of the rate of occupying for the whole volume, and voidage here puts rates of the volume other than structures, such as an active material, an electric conduction agent, and a binder. When voidage is less than 15%, an elevated-temperature preservation property becomes good, but since a touch area with the electrolytic solution decreases too much, a discharge property falls. Moreover, when voidage exceeds 40%, the electronic conduction nature of an electrode is easy to be spoiled, and the cell property after being saved under the elevated temperature a discharge property's not only not being improved, but falls remarkably. As explained above, the optimal balance which also makes an elevated-temperature preservation property good exists in selection of the BET specific surface area resulting from primary particle size, the secondary particle size which is the floc, and the voidage of a paint film, making a discharge property good, and balance will become good if it is the combination of the range of this invention.

[0011] The manganese raw material of the lithium manganese multiple oxide used for this invention can mention EMD (Electrolytic Manganese Dioxide), CMD (Chemical Manganese Dioxide), gamma-MnOOH, and MnCO₃ as an example. As a lithium raw material, although Li₂CO₃, LiOH, LiNO₃, CH₃COOLi, etc. can be mentioned as an example, Li₂CO₃ is desirable. The lithium manganese multiple oxide used for this invention is obtained as follows, for example. After mixing the mixture of EMD ground so that mean particle diameter might be set to 5-30 micrometers, and Li₂CO₃ so that a Li/Mn ratio may be set to 0.5, heat treatment of 10 hours or more is performed at 800-950 degrees C among atmospheric air. After cooling to near a room temperature, it can obtain by adding and mixing and performing still more preferably 400-700 degrees C of heat treatments of 10 hours or more at 500-650 degrees C so that it may become the Li/Mn ratio of the request of Li₂CO₃ to this. Moreover, if another example is given, after mixing a raw material by the desired Li/Mn ratio beforehand and performing heat treatment of 10 hours or more at 800-950 degrees C among atmospheric air, 400-700 degrees C of heat treatments of 10 hours or more may be again carried out at 500-700 degrees C still more preferably.

[0012] In order to make specific surface area below into 1.5m²/g, the 1st needs to be heat-treated [800-900-degree C]. Furthermore, it is important to perform 2nd heat treatment, and unless it performs 2nd heat treatment, it is easy to remain and is not desirable [any phases other than the purposes, such as Li₂MnO₃ and Mn₃O₄,]. Therefore, although the 2nd heat treatment is more than the decomposition temperature of Li₂MnO₃ or Mn₃O₄, it has desirable extent that it is the range of 500-700 degrees C so that manganese and a lithium can be permuted enough.

[0013] Measurement of the presentation in this invention, specific surface area and voidage, and mean particle diameter is explained. After the presentation checked first that it was a single phase by X diffraction measurement, it was dissolved with the hydrochloric acid which heated the sample. The total amount of Mn and the total amount of Li(s) were calculated using ICPS-1000III by Shimadzu Corp. which is RF plasma-emission-spectrometry equipment (ICP) from this solution. Next, JISK1467 (1984) was asked for MnO₂ amount by the approach of a publication, and count determined the presentation from these results. Measurement of the specific surface area by the BET adsorption method was performed with the one point method for BET method using nitrogen gas using Gemini 2360 by Shimadzu Corp. Moreover, the pore sizer 9320 by Shimadzu Corp. was used for measurement of voidage. The mean particle diameter of an aggregated particle was measured using what used together RODOS of a dry type distributed system to the HELOS system by JEOL Co., Ltd. Magnitude of primary particle size was considered as the average of the magnitude of ten primary particles obtained by the typical visual field with the scanning electron microscope of S-800 mold by Hitachi, Ltd. Next, the creation approach of a nonaqueous electrolyte rechargeable battery is explained. It mixes with powder with electronic conduction nature, and the obtained lithium manganese multiple oxide is fixed to the current collection material of aluminum with a binder. Since the addition of an electric conduction agent and a binder affects the voidage of a positive electrode, it is desirable to add a necessary minimum amount. As an example of an electric conduction agent, although a natural graphite, an artificial graphite, carbon black, KETCHIEN black, and acetylene black can be mentioned, concomitant use of a graphite or a graphite, and acetylene black is desirable. In order to maintain electronic conduction nature as the addition, 1 - 20 % of the weight is 5 - 15 % of the weight desirable still more preferably. It is not desirable in order for the capacity per unit volume to fall, when conductivity does not become homogeneity for it to be less than 1 % of the weight, but 20 % of the weight was exceeded and a required opening is secured. moreover, to a binder, Pori ethylene tetrafluoride, polyvinylidene fluoride, an ethylene-propylene-diene

terpolymer; a carboxymethyl cellulose, styrene butadiene rubber, a fluororubber, etc. are usually independent -- or it is not limited, especially although it is mixed and is used. As these additions, 1 - 10 % of the weight is 2 - 5 % of the weight desirable still more preferably. At less than 1 % of the weight, binding capacity is weak, and while checking migration of Li ion in the case where 10 % of the weight is exceeded, since it is hard coming to secure a required opening, it is not desirable. Pressing of the obtained positive electrode is carried out with the roll press machine heated to the temperature of about 150 degrees C a room temperature or if needed, and an electrode with desired voidage is obtained.

[0014] As a negative-electrode active material ingredient used for this invention, especially if the occlusion emission of the lithium can be carried out in an ionic state, it will not be limited, but although carbon materials, such as corks, a natural graphite, an artificial graphite, and difficulty graphitized carbon, the metallic oxide of SiSnO_3 grade, and the metal nitride of LiCoN_2 grade can be mentioned as an example, in order to make high the average electrical potential difference at the time of discharge, it is a graphite ingredient preferably [it is desirable and] to a carbon material and a pan.

[0015] When electrode-izing a negative-electrode active material, an electric conduction agent can be added if needed and it can fix to current collection material with a binder. As an example of an electric conduction agent, a natural graphite, an artificial graphite, carbon black, KETCHIEN black, and acetylene black can be mentioned. Although not limited especially as the addition, 10 or less % of the weight is 5 or less % of the weight desirable still more preferably. If 10 % of the weight is exceeded, the effect of the charge-and-discharge capacity of an electric conduction agent or current efficiency becomes large and is not desirable. moreover, to a binder, Pori ethylene tetrafluoride, polyvinylidene fluoride, an ethylene-propylene-diene terpolymer, a carboxymethyl cellulose, styrene butadiene rubber, a fluororubber, etc. are usually independent -- or although it is mixed and is used, it is not limited especially. As these additions, 1 - 20 % of the weight is 1 - 10 % of the weight desirable still more preferably. At less than 1 % of the weight, binding capacity is weak, in the case where 20 % of the weight is exceeded, migration of Li ion is checked and the engine performance as a cell falls.

[0016] Moreover, what was dissolved in the non-aqueous solvent by using lithium salt as an electrolyte is used for the nonaqueous electrolyte used by this invention. As an electrolyte, although LiClO_4 , LiPF_6 , LiBF_4 , and LiCF_3SO_3 grade are mentioned, for example, especially LiPF_6 and LiBF_4 are desirable. As a non-aqueous solvent, although carbonate, lactone, ether, etc. are mentioned, carbonate, such as ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, and methylethyl carbonate, is especially desirable. To a solvent, independent or the electrolytic concentration which can use two or more kinds of partially aromatic solvents, and is dissolved in these solvents has the desirable range of 0.5-2.0 mols/l. in these. In separating from this range, the ion conductivity of the electrolytic solution falls and the engine performance of a cell falls.

[0017]

[Embodiment of the Invention] Hereafter, although this invention is further explained to a detail based on an example, this invention is not limited to the following example.

[0018]

[Example 1] EMD with a mean particle diameter of 20 micrometers and Li_2CO_3 were mixed by the presentation ratio of $\text{Li}/\text{Mn}=0.50$ as a start raw material, and after heat-treating at 850 degrees C among air for 20 hours, it cooled to near a room temperature. Subsequently, the thing and Li_2CO_3 which were obtained were mixed so that it might become the presentation ratio of $\text{Li}/\text{Mn}=0.64$, and the lithium manganese multiple oxide was again obtained by heat-treating at 650 degrees C among air for 12 hours. As a result of performing a chemical analysis, the obtained lithium manganese multiple oxide was presumed to be $\text{Li}[\text{Li}_{0.14}\text{Mn}_{1.86}] \text{O}_4$, the BET specific surface area was $0.69\text{m}^2/\text{g}$, and the mean particle diameter of an aggregated particle was 21 micrometers. Moreover, the mean particle diameter of a primary particle was 1.3 micrometers.

[0019] The concrete cell creation in this invention is explained. After mixing the acetylene black 3 weight section and the lepidic form natural-graphite 3 weight section as an electric conduction agent to the above-mentioned lithium manganese multiple oxide 100, to AUW, at a rate of 3 weight sections, polyvinylidene fluoride was mixed and N methyl pyrrolidone (NMP) addition was carried out, and wet blending was performed and it considered as the paste. Subsequently, this paste was applied to both sides of aluminium foil with a thickness of 20 micrometers it is thin to a positive-electrode charge collector at homogeneity, and after making it dry, the positive electrode band-like by carrying out pressing with the roller press machine heated at 150 degrees C was created. The voidage of the electrode at this time was 21%.

[0020] Next, to the mixture of 95 % of the weight of meso carbon fibers, and 5 % of the weight of lepidic form natural graphites graphitized at 3000 degrees C, purified water was added as the carboxymethyl-cellulose 1 weight

section, the styrene-butadiene-rubber 2 weight section, and a solvent, wet blending was performed, and it considered as the paste. This paste was applied to both sides of copper foil with a thickness of 12 micrometers it is thin to a negative-electrode charge collector at homogeneity, and after making it dry, the negative electrode band-like by carrying out pressing with a roller press machine was created. Furthermore, it considered as the roll-like object by winding in the shape of a roll on both sides of the polyethylene fine porosity film of 25-micrometer thickness as a separator between the above-mentioned positive electrode and the above-mentioned negative electrode.

[0021] The insulating film was inserted in the pars basilaris ossis occipitalis of an iron cylinder can which performed nickel plating, and said roll-like object was inserted. Subsequently, the negative-electrode tab picked out from the roll-like object was welded to the can bottom, and the positive-electrode tab was welded to the gasket, the explosion-proof disk, and the lock out lid that consists of a PTC component. After pouring in the electrolytic solution which dissolved LiPF₆ in the mixed solvent of ethylene carbonate and diethyl carbonate by the concentration of one mol/l. and inserting an insulating film into a cell can in the roll-like object upper part, said lock out lid was put in and the cylindrical nonaqueous electrolyte rechargeable battery with a 17mm height [of appearances] of 500mm was created by closing the edge of a cell can.

[0022]

[Example 2] The lithium manganese multiple oxide was obtained by mixing EMD with a mean particle diameter of 5 micrometers and Li₂CO₃ by the presentation ratio of Li/Mn=0.56 as a start raw material, heat-treating at 900 degrees C among air for 20 hours, and subsequently heat-treating at 600 degrees C for 20 hours. As a result of performing a chemical analysis, the obtained lithium manganese multiple oxide was presumed to be Li [Li_{0.06}Mn_{1.94}] O₄, and the BET specific surface area was 0.31m²/g. Moreover, the mean particle diameter of the aggregated particle after composition was 6.8 micrometers. The mean particle diameter of a primary particle was 2.7 micrometers. The nonaqueous electrolyte rechargeable battery was created by the same approach as an example 1 using the obtained lithium manganese multiple oxide. The voidage of the electrode at this time was 32%.

[0023]

[The example 1 of a comparison] The nonaqueous electrolyte rechargeable battery was created by the same approach as an example 1 using the lithium manganese multiple oxide obtained in the example 1 except having created the electrode whose voidage is 11%.

[0024]

[The example 2 of a comparison] The nonaqueous electrolyte rechargeable battery was created like the example 2 using the lithium manganese multiple oxide obtained in the example 2 except having created the electrode whose voidage is 44%.

[0025]

[The example 3 of a comparison] It mixed with the ball mill by the presentation ratio of Li/Mn=0.52 for 24 hours, using MnCO₂ with a mean particle diameter of 0.5 micrometers and LiOH as a start raw material. Subsequently, the lithium manganese multiple oxide was obtained by heat-treating at 600 degrees C among air for 12 hours. The obtained lithium manganese multiple oxide was presumed to be Li [Li_{0.03}Mn_{1.97}] O₄ as a result of the chemical analysis, the BET specific surface area was 2.6m²/g, and the mean particle diameter of an aggregated particle was 0.82 micrometers. Moreover, the mean particle diameter of a primary particle was 0.2 micrometers. The electrode of 35% of voidage was created using the obtained lithium manganese multiple oxide, and the nonaqueous electrolyte rechargeable battery was created like the example 1.

[0026]

[The example 4 of a comparison] EMD with a mean particle diameter of 5 micrometers and Li₂CO₃ were mixed by the presentation ratio of Li/Mn=0.56 as a start raw material, and the lithium manganese multiple oxide was obtained by heat-treating at 600 degrees C among air for 20 hours. As a result of performing a chemical analysis, the obtained lithium manganese multiple oxide was presumed to be Li [Li_{0.06}Mn_{1.94}] O₄, and the BET specific surface area was 1.8m²/g. Moreover, the mean particle diameter of the aggregated particle after composition was 5.3 micrometers. Although particle diameter was not able to be concluded since the configuration of a primary particle did not clarify by scanning electron microscope observation, either, it was 0.1 micrometers about. The nonaqueous electrolyte rechargeable battery was created by the same approach as an example 1 using the obtained lithium manganese multiple oxide. The voidage of the electrode at this time was 26%.

[0027] (Test result) It set the charge electrical potential difference as 4.2V, and charged in 5 hours after each cell created in the above-mentioned examples 1 and 2 and the examples 1, 2, and 3 of a comparison passed the aging

period of 24 hours for the purpose of the stabilization inside a cell. Subsequently, the charge-and-discharge cycle which discharges to 2.7V with a 350mA (an equivalent for 0.5C [About]) fixed current, and discharges with the current value of 0.5C to charge and 2.7V by 4.2V setup in 3 hours for the further stabilization was used as the trial cell after 5 cycle *****.

[0028] The charge electrical potential difference was set as 4.2V, it charged in 3 hours, and the discharge property measured discharge quantity of electricity by discharging with the current value equivalent to 0.5C, and 1C, 2C and 3C. The discharge property of each cell made 100% discharge quantity of electricity in the current value equivalent to 0.5C, and computed it as a relative value. Subsequently, it is two-cycle ***** about the charge-and-discharge cycle which discharges with the current value of 0.5C to charge and 2.7V by 4.2V setup in 3 hours. Last discharge quantity of electricity at this time was made into the criteria discharge capacity (X) of each trial cell. It took out, 24 hours after putting each cell into the thermostat set as 85 degrees C furthermore. After being cooled naturally to near a room temperature, the taken-out cell discharged to 2.7V and, subsequently performed 4.2V charge and 2.7V discharge. The latter amount of discharge was made into the recovery discharge capacity (Y) of a trial cell. Based on these, the capacity recovery factor after preservation of each cell was computed according to the degree type.

[0029] $(Y/X) \times 100$ [0030]

[Table 1]

	実施例 1	実施例 2	比較例 1	比較例 2	比較例 3	比較例 4
BET比表面積 (m^2/g)	0.69	0.31	0.69	0.31	2.6	1.8
二次粒径(μm)	21	6.8	21	6.8	0.82	5.3
一次粒径(μm)	1.3	2.7	1.3	2.7	0.2	0.1
空隙率(%)	21	32	11	44	35	26
放電特性	0.5C	100%	100%	100%	100%	100%
	1.0C	99%	66%	99%	98%	99%
	2.0C	79%	23%	80%	81%	78%
保存特性	3.0C	52%	14%	42%	46%	43%
	容量回復率	83%	74%	54%	0%	37%

[0031] If voidage of the positive electrode with which the mean diameter of an aggregated particle used further 5-30 micrometers of lithium manganese multiple oxides for specific surface area below 1.5m²/g is made 20 - 35% as shown in Table 1, the discharge property of a cell can obtain a nonaqueous electrolyte rechargeable battery also with the good preservation property under an elevated temperature good.

[0032]

[Effect of the Invention] According to this invention, the mean particle diameter of a primary particle specific surface area below 1.5m²/g 0.5-5 micrometers, When the mean particle diameter of an aggregated particle uses 5-30 micrometers as the nonaqueous electrolyte rechargeable battery using the positive electrode with which the lithium manganese multiple oxide of a spinel system was supported as an active material which made voidage of an electrode further 15 - 40% of range The discharge property of a cell is also good, and since the irreversible capacity fall of a cell decreases sharply even if saved at an about 80-degree C elevated temperature, a highly efficient nonaqueous electrolyte rechargeable battery can be cheap, it can supply now, and the industrial value is very large.

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